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ACTIVATED CARBON FABRIC FROM PITCH

by

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Union Carbide Corporation
Carbon Products Division

Approved for public release;
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A project was undertaken to determine whether pitch-based carbon cloth could be made into an active cloth suitable for clothing protective against hazardous chemical environments. The experiments involved activating pitch-based cloth by standard methods in steam and CO_2 in a laboratory reactor. Cloth with sorptivities exceeding 50% CCl_4 by weight, surface areas exceeding 800 m^2/gm, and breaking strengths exceeding 5 kg per 25 mm wide strip were produced. Conditions were optimized to produce cloth of the highest area sorptivities for NARADCOM evaluation.

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PREFACE

For several years, the Army has been interested in the fabrication of experimental protective clothing containing activated carbon yarn or fabric. The activiated carbon fabric was available only from foreign sources. The carbon yarn used came from a domestic source but was made from a viscose rayon precursor yarn which is no longer being manufactured. When the manufacturer announced cessation of production, personnel at the U.S. Army Natick Research and Development Command (NARADCOM) recognized that, if this portion of the Army's research program were to continue, a new precursor yarn must be developed. It was also recognized that a domestic source of activated carbon fabric was desirable. One of the possible materials suitable for activated carbon yarn and fabric development was petroleum pitch. Investigation of this material indicated that a process for spinning pitch-based fibers had been developed exclusively in this country by Union Carbide Corporation and that preoxidized and graphitized pitch-based materials were available. Discussions were held with representatives of Union Carbide Corporation regarding the Army's interest and, as a result, a few fabric samples were prepared which showed promise of satisfactory activation. This effort indicated that fabric would be easier than yarn to process in the initial development of activated carbon textiles, and a contract scope of work was written with this objective. Initial technical discussions were held with Dr. Herbert Volk of Union Carbide. Subsequently, the contract effort was turned over to Mr. S. M. Boszor as Principal Investigator. Dr. Richard N. Macnair was the Project Officer for NARADCOM.

FIGURES

TABLES

ACTIVATED CARBON FABRIC FROM PITCH

I. SUMMARY AND CONCLUSIONS

The objectives of the contract were:

1. To determine if carbon cloth made from pitch-based yarn could be activated using common techniques;
2. If so, to determine the optimum process conditions under which to make the activated carbon cloth; and
3. To determine the characteristic properties of the cloth so produced.

Additionally, goals for CCl_4 vapor sorption (50%), breaking strength (2 kg per 25 mm width), surface area (800 m^2/gm), and pore size distribution (<50Å diameter for majority of pores) were set.

All of the objectives and goals were met during the course of the experimental work. It was demonstrated that pitch-based carbon cloth activated in a laboratory rotary reactor under a steam atmosphere for about 30 minutes at about 875°C had the necessary characteristics. A self-directing optimization scheme was used to determine optimum process conditions.

II. BACKGROUND

Fabrics containing activated carbon are needed for the manufacture of clothing which will protect wearers against hazardous chemical vapors.[1,2] The fabrics currently used contain powdered active carbon

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[1] Richard N. Macnair and Gilbert N. Arons, "Sorptive Textile Systems Containing Activated Carbon Fibers", in Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, c1978.

[2] Gilbert N. Arons, Richard N. Macnair, Laurance G. Coffin, and Hubertina D. Hogan, "Sorptive Textile Systems Containing Activated Carbon Fibers", Textile Research Journal, November, 1974.

bonded to a substrate such as polymer foam. The fabrics so produced are relatively heavy and insulative. Lighter and more comfortable fabrics for clothing were sought, and activated carbon yarn was potentially attractive as a fabric material.

It was reported in the Technical Proposal (PTC-7805-1) upon which this contract was based that pitch-based yarn made by Union Carbide Corporation developed some increased surface area (350 to 600 m^2/gm) and CCl_4 activity (22 to 34% by weight) in some exploratory experiments. Pitch-based fibers appeared to have the potential to yield effective activated carbon yarn and cloth for protective clothing applications.

One objective of the technical effort under this contract was to demonstrate a process for making activated carbon cloth from a pitch-yarn precursor. The process was to have demonstrated reproducibility, and samples of the best cloth produced under the contract were to be delivered to the United States Army Natick Research and Development Command (NARADCOM) for evaluation.

The performance goals of the contract were as follows:

1. Sorption of saturated CCl_4 vapor on a weight basis - 50% minimum.
2. Grab breaking strength - 2 kg minimum on 25 mm width in warp and fill directions.
3. Surface area (N_2 BET method) - 800 m^2/gm minimum.
4. Pore distribution (N_2 BET method) - majority of pores less than 50Å diameter.

The contract was amended to add an optimization study which had the goal of optimizing the process conditions to produce samples which would provide maximum sorptivity as determined by NARADCOM testing. Samples produced under optimum process conditions were then to be sent to NARADCOM for evaluation.

A lightweight plain weave cloth with 16 yarns per inch in the warp direction and 14 yarns per inch in the fill direction which had been woven from 2000 filament pitch-based thermoset yarn produced by Union Carbide Corporation[3,4,5] was chosen as the experimental material upon which to do the activation experiments. The cloth was woven by Fabric Development, Inc., of Quakertown, Pennsylvania. The woven fabrics were preactivated at three heating rates to three final temperatures for a total of nine separate starting materials. The preactivation heat treatment conditions were proprietary to Union Carbide.

III. LABORATORY EQUIPMENT AND METHODS

The activations were done in a laboratory rotary reactor. Figures 1 and 2 are sketches of the apparatus. The maximum sample width which could be loaded into the activation screen tube was 150 mm. The length of the sample was 300 mm. In order to load this size sample into the screen tube, the cloth was coiled as shown in Figure 3. The coiling resulted in a permanent set being imparted to the final sample. The width of the sample was taken in the warp direction of the starting fabric. The reaction vessel was rotated at 11 rpm while the activations were in progress. A "flame curtain" was provided at the encrance to the furnace to prevent unwanted oxygen from entering and to provide some preheating for the incoming gases.

The furnace was preheated to the operating temperature of each run before the reactor containing the sample was inserted. When the sample was inserted, nitrogen gas (4 liters per minute) was provided to the reaction chamber. The nitrogen was continued until the chamber had reached the desired process temperature. Either water (6 cc per minute) or CO_2 (11 liters per minute) was introduced to the reactor along with

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[3] U.S. Patent No. 4,005,183, "High Modulus, High Strength Carbon Fibers Produced from Mesophase Pitch" by L. S. Singer.

[4] U.S. Patent No. 4,138,525, "Highly Handleable Pitch-Based Fibers", by D. A. Schulz.

[5] U.S. Patent No. 4,014,725, "Method of Making Carbon Cloth from Pitch-Based Fiber", by D. A. Schulz.

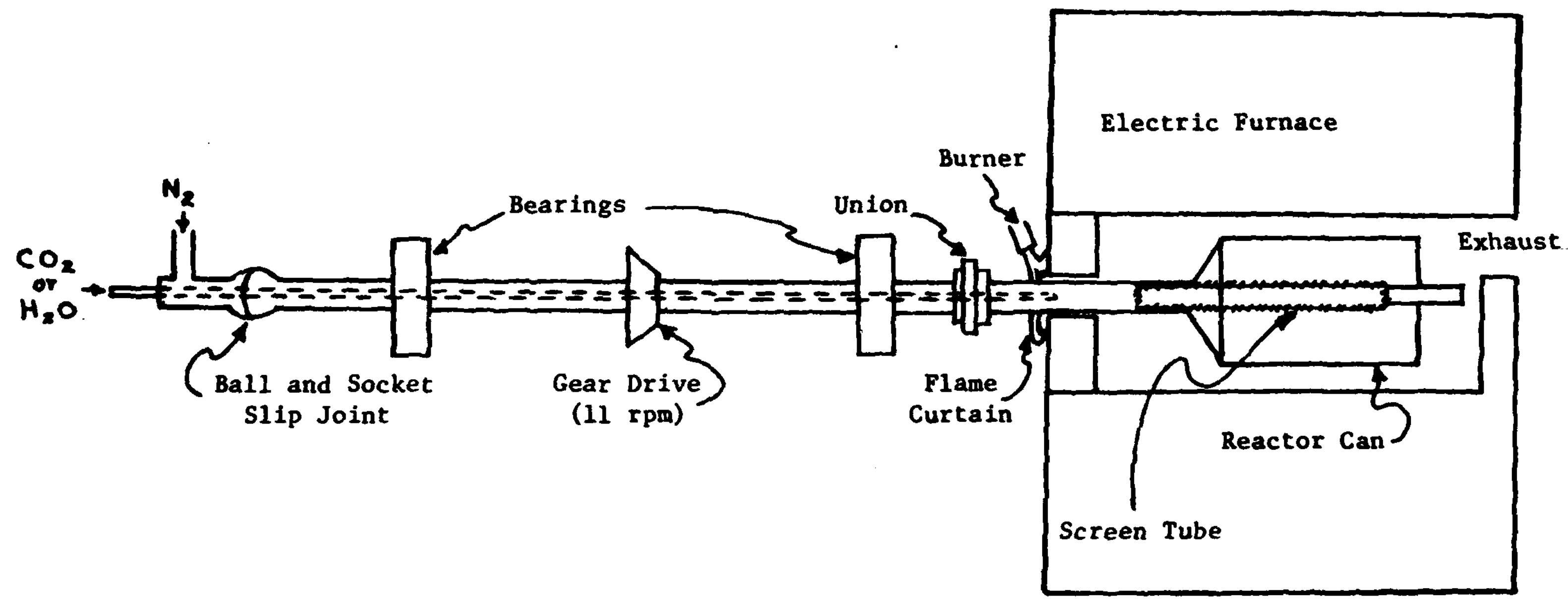

Figure 1. Rotary Activator

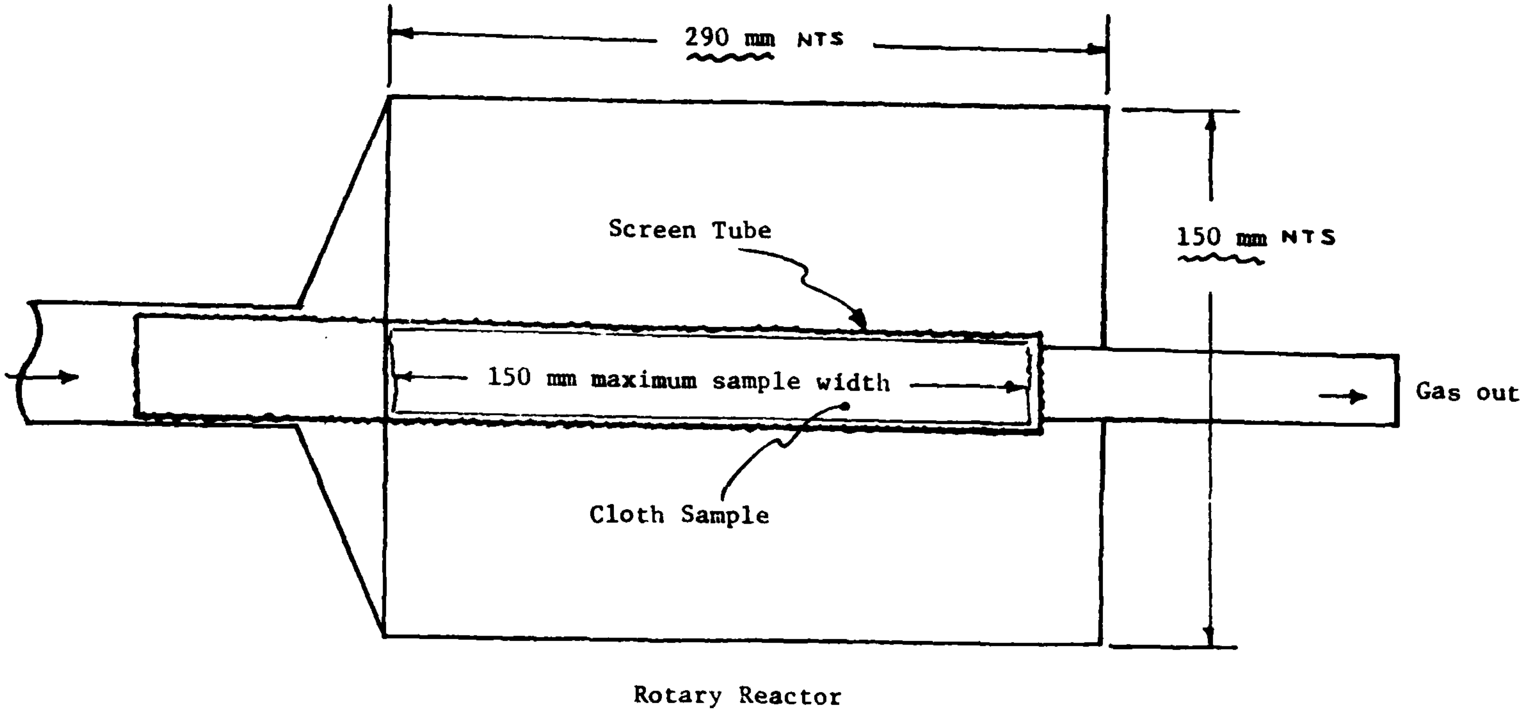

Figure 2. Detail of Rotary Reaction Vessel

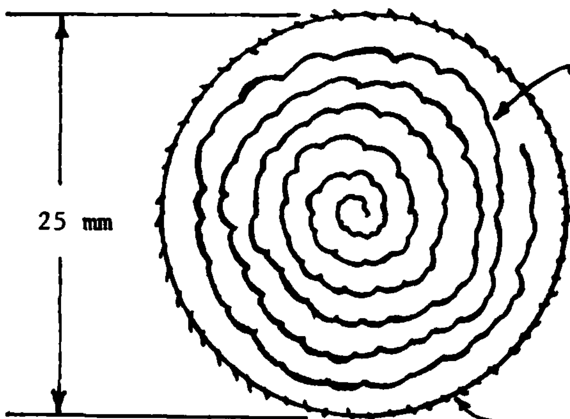

Figure 3. End View of Sample Coiled Inside Screen Tube

the nitrogen. The flow of gases was continued until the desired reaction time had expired. The reactor was then removed from the furnace, and the furnace, and the CO_2 or water was shut off; but the nitrogen flow was continued until the reactor had cooled.

The sorptivities of the samples were determined according to ASTM D-3467.[6] Samples approximately 30 x 120 mm were used for the determinations. For the optimization study, sample sizes were carefully determined and the weight pickup of CCl_4 was calculated in grams adsorbed per square centimeter of sample (area basis) as well as grams adsorbed per gram sample (weight basis).

The breaking strength was determined by pulling to failure a 25 mm wide strip of cloth with the tensile force being applied in the warp direction. The gauge length was taken as 75 mm and three strips were tested per sample. Only the warp direction was tested. The breaking strengths generally encountered were so many times more than the minimum desired strength that further testing was considered unnecessary.

Total sample surface areas (N_2 BET) were determined on a "Digisorb 2500" surface area and pore volume analyzer made by Micromeritics Instrument Corporation. Approximately one-gram samples were tested. The determinations required extensive waiting periods (in some cases periods of several days) for equilibration and, therefore, surface area determinations were excluded from the optimization study. Pore size distributions were determined during the same tests.

IV. FEASIBILITY STUDY

A. Experimental Matrix

The nine samples which had been preactivated were evaluated for surface area development by the N_2 BET test. The results are shown

[6] ANSI/ASTM D-3467-76, "Standard Test Method for Carbon Tetrachloride Activity of Activated Carbon", American Society for Testing and Materials.

in Table 1. Samples numbered 2, 5, and 8 showed the highest surface areas and were selected for further work. One kilogram samples were made at each of the same conditions at which Nos. 2, 5, and 8 were made and were numbered materials 10, 11, and 12, respectively. Reproducibility runs of one kilogram each were also made at the same respective conditions and were numbered materials 13, 14, and 15, respectively.

The chosen materials were arranged in a matrix of activation conditions as shown in Table 2. The sample numbers indicate the history of each sample. The first two digits are the starting material, the third digit is the relative temperature of activation, the fourth digit is the relative activation time, and the final letter or group of letters indicates the activation atmosphere. Example: 1022S represents material No. 10 activated to the second level temperature (900°C) for the second level time (40 minutes) in a steam atmosphere.

B. Results of Matrix Runs

Tables 3, 4, and 5 show the results of all the runs made to fill the original matrix. Figures 4, 5, and 6 present these data graphically. The most promising samples produced during the trials were those made at 900°C for 40 minutes in a steam atmosphere (1022S, 1122S, and 1222S). These samples were made under intermediate conditions and were, therefore, chosen to be characterized for strength and surface area. The results of those tests satisfied the original contract goals. The starting materials apparently made little difference.

Reproducibility runs were made at the most promising conditions. Table 6 gives a summary of the properties of these samples. It was apparent that the properties of these samples exceeded the minimum goals of the contract. It was, therefore, decided to optimize the activation conditions to produce the best possible material from the pitch-based precursor.

TABLE 1

SURFACE AREAS OF PREACTIVATED SAMPLES

Sample Number	Heating Rate	Final Temperature	N_2 BET Surface Area (m^2/gm)
1	Low	Low	2
2	Medium	Low	20
3	High	Low	1
4	Low	Medium	3
5	Medium	Medium	330
6	High	Medium	2
7	Low	High	4
8	Medium	High	340
9	High	High	10

TABLE 2

ACTIVATION CONDITIONS COVERED BY EXPERIMENTAL MATRIX

Starting Material	Low Temperature Preactivated				Medium Temperature Preactivated				High Temperature Preactivated		
Sample Number	Atmos.	Temp. (°C)	Time (Min.)	Sample Number	Atmos.	Temp. (°C)	Time (Min.)	Sample Number	Atmos.	Temp. (°C)	Time (Min.)
1011S	Steam	850	20	1111S	Steam	850	20	1211S	Steam	850	20
1012S			40	1112S			40	1212S			40
1013S			60	1113S			60	1213S			60
1021S		900	20	1121S		900	20	1221S		900	20
1022S			40	1122S			40	1222S			40
1023S			60	1123S			60	1223S			60
1031S		950	20	1131S		950	20	1231S		950	20
1032S			40	1132S			40	1232S			40
1033S			60	1133S			60	1233S			60
$1011CO_2$	CO_2	850	20	$1111CO_2$	CO_2	850	20	$1211CO_2$	CO_2	850	20
$1012CO_2$			40	$1112CO_2$			40	$1212CO_2$			40
$1013CO_2$			60	$1113CO_2$			60	$1213CO_2$			60
$1021CO_2$		900	20	$1121CO_2$		900	20	$1221CO_2$		900	20
$1022CO_2$			40	$1122CO_2$			40	$1222CO_2$			40
$1023CO_2$			60	$1123CO_2$			60	$1223CO_2$			60
$1031CO_2$		950	20	$1131CO_2$		950	20	$1231CO_2$		950	20
$1032CO_2$			40	$1132CO_2$			40	$1232CO_2$			40
$1033CO_2$			60	$1133CO_2$			60	$1233CO_2$			60

TABLE 3

ACTIVITIES AND YIELDS OF ACTIVATED LOW TEMPERATURE PREACTIVATED CLOTH SAMPLES

Sample Number	Atmos.	Time (Min.)	Temp. (°C)	CCl_4 Sorptivity[1] (% by Weight)	Surface[2] Area (m^2/gm)	Percent[3] Yield	Strength[4] (kg)
1011S	Steam	20	850	19.7		63.7	
1012S		40		49.3		44.3	
1013S		60		57.9		32.4	
1021S		20	900	36.1		55.4	
1022S		40		64.5	950	29.3	6.8
1023S		60		71.6		21.8	
1031S		20	950	51.6		40.2	
1032S		40		74.8		12.6	
1033S		60		101.6		2.9	
$1011CO_2$	CO_2	20	850	0.0		78.4	
$1012CO_2$		40		0.10		75.3	
$1013CO_2$		60		0.14		76.2	
$1021CO_2$		20	900	0.2		76.4	
$1022CO_2$		40		6.2		70.5	
$1023CO_2$		60		6.3		69.6	
$1031CO_2$		20	950	2.3		74.6	
$1032CO_2$		40		7.5		70.2	
$1033CO_2$		60		17.0		62.1	

(1) ASTM D-3467
(2) N_2 BET
(3) Weight carbon after activation divided by weight carbon initially times 100%.
(4) Tested on 25 mm wide strips in warp direction.

TABLE 4

ACTIVITIES AND YIELDS OF ACTIVATED MEDIUM TEMPERATURE PREACTIVATED CLOTH SAMPLES

Sample Number	Atmos.	Time (Min.)	Temp. (°C)	CCl_4 Sorptivity(1) (% by Weight)	Surface(2) Area (m^2/gm)	Percent(3) Yield	Strength(4) (kg)
1111S	Steam	20	850	17.8		71.4	
1112S		40		39.4		53.2	
1113S		60		52.1		41.4	
1121S		20	900	39.1		54.7	
1122S		40		60.6	982	36.4	9.9
1123S		60		80.1		19.6	
1131S		20	950	46.7		49.6	
1132S		40		81.3		17.5	
1133S		60		115.2		1.7	
$1111CO_2$	CO_2	20	850	0.0		85.0	
$1112CO_2$		40		0.0		83.8	
$1113CO_2$		60		0.13		81.4	
$1121CO_2$		20	900	0.33		83.0	
$1122CO_2$		40		0.87		81.1	
$1123CO_2$		60		5.30		77.8	
$1131CO_2$		20	950	1.7		80.7	
$1132CO_2$		40		7.1		76.4	
$1133CO_2$		60		14.1		70.8	

(1) ASTM D-3467
(2) N_2 BET
(3) Weight carbon after activation divided by weight carbon initially times 100%.
(4) Tested on 25 mm wide strips in warp direction.

TABLE 5

ACTIVITIES AND YIELDS OF ACTIVATED HIGH TEMPERATURE PREACTIVATED CLOTH SAMPLES

Sample Number	Atmos.	Time (Min.)	Temp. (°C)	CCl_4 Sorptivity(1) (% by Weight)	Surface(2) Area (m^2/gm)	Percent(3) Yield	Strength(4) (kg)
1211S	Steam	20	850	11.6		77.1	
1212S		40		54.2		45.9	
1213S		60		69.6		31.8	
1221S		20	900	37.2		61.9	
1222S		40		64.5	912	37.3	12
1223S		60		84.5		13.3	
1231S		20	950	50.8		47.5	
1232S		40		75.2		23.5	
1233S		60		Burned up		0	
$1211CO_2$	CO_2	20	850	0.0		93.9	
$1212CO_2$		40		0.0		87.5	
$1213CO_2$		60		4.3		83.1	
$1221CO_2$		20	900	0.39		87.6	
$1222CO_2$		40		4.40		84.3	
$1223CO_2$		60		7.10		81.8	
$1231CO_2$		20	950	2.4		85.7	
$1232CO_2$		40		9.3		79.6	
$1233CO_2$		60		15.6		74.4	

(1) ASTM D-3467
(2) N_2 BET
(3) Weight carbon after activation divided by weight carbon initially times 100%.
(4) Tested on 25 mm wide strips in warp direction.

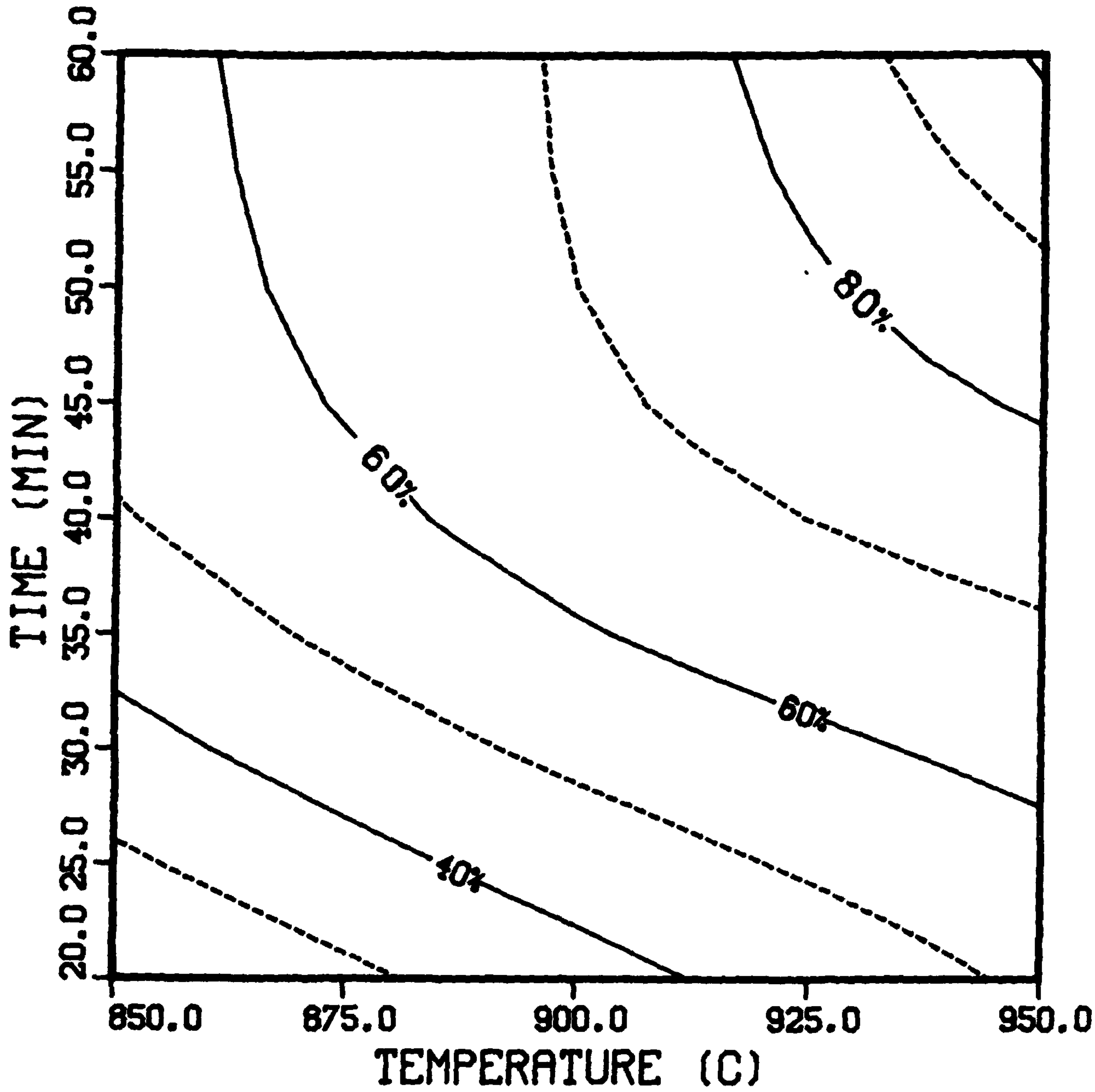

Figure 4.

ASTM D3467 Wgt. % CCl_4 Sorptivity

Steam Activation of #10 Material

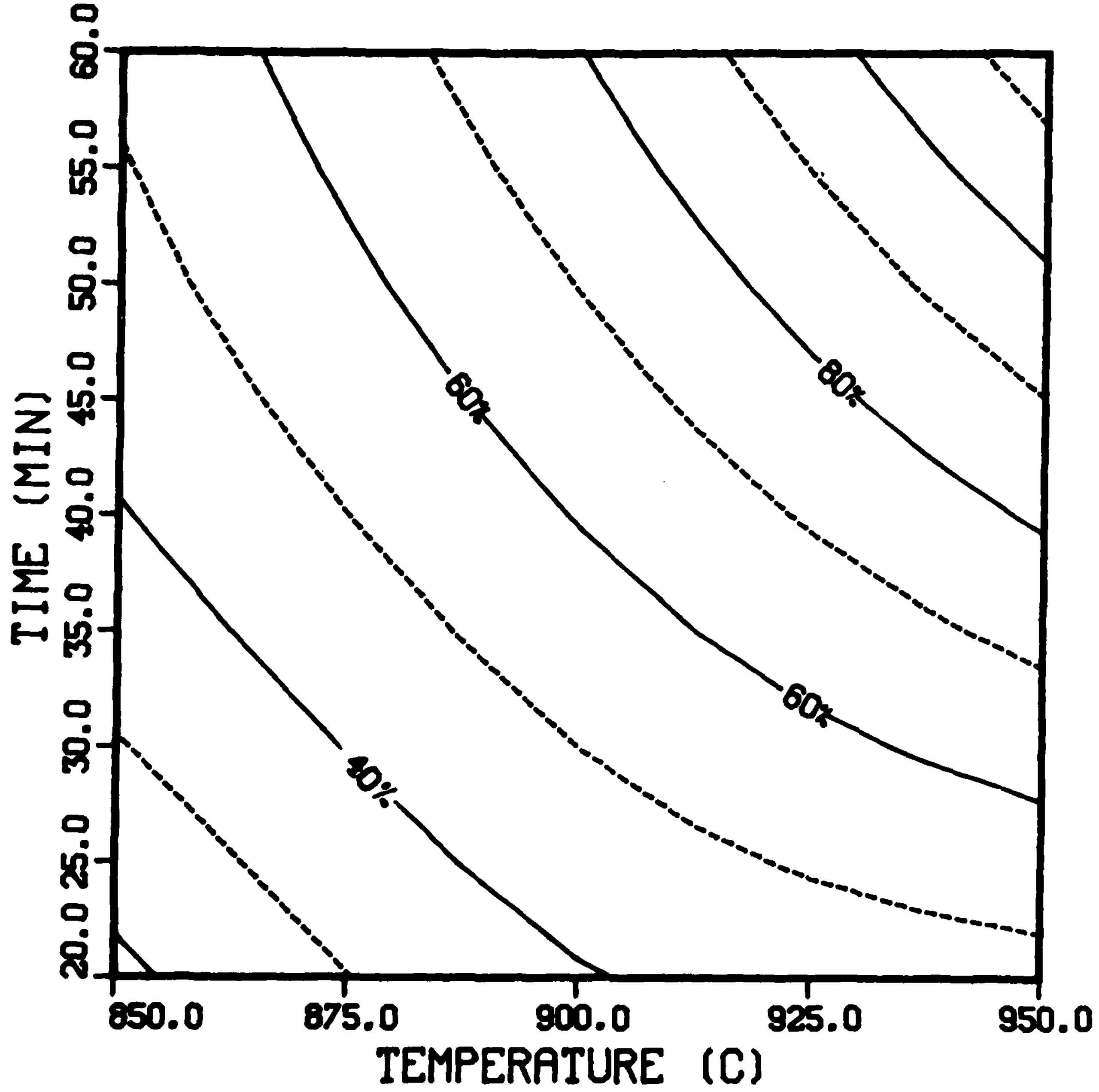

Figure 5.

ASTM D3467 Wgt. % CCl_4 Sorptivity

Steam Activation of #11 Material

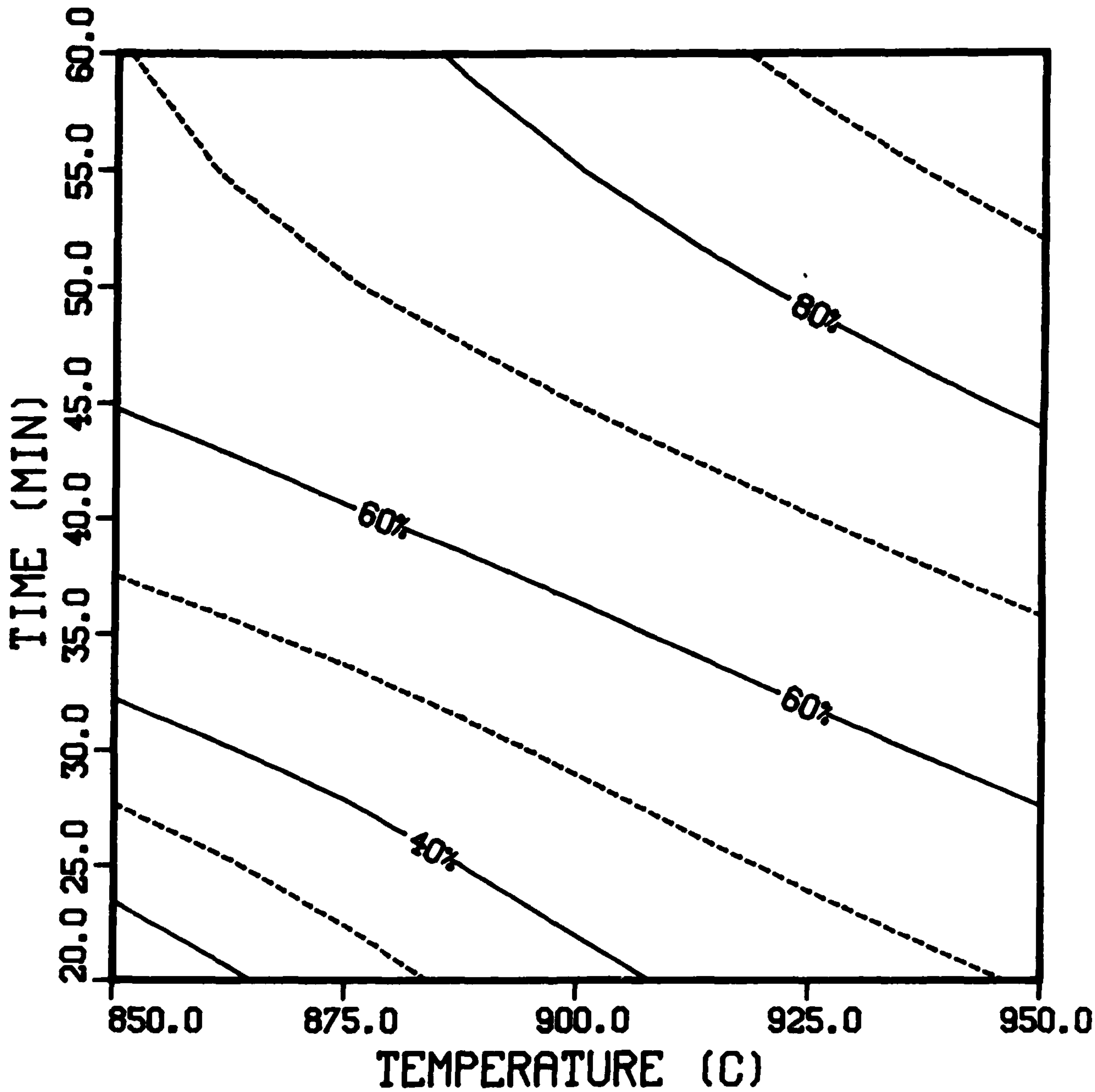

Figure 6.

ASTM D3467 Wgt. % CCl_4 Sorptivity

Steam Activation of #12 Material

TABLE 6

SUMMARY OF PROPERTIES OF "MOST PROMISING" ACTIVATED CARBON CLOTH SAMPLES

	Contract Minimum Goals	Low Temperature Preactivated		Medium Temperature Preactivated		High Temperature Preactivated	
		1022S	1322S*	1122S	1422S*	1222S	1522S*
CCl_4 Sorption (ASTM D-3467)	50% by weight	63.6	64.7	71.4	66.5	69.1	51.1
Breaking Strength	2 Kg	6.8 (warp)	(1)	9.9 (warp)	(1)	12 (warp)	(1)
Surface Area	800 m^2/gm	950	833	982	853	912	810
Pore Size Distribution	Majority <50 A	(2)	96% <50 A	(2)	99% <50 A	(2)	96% <50 A

(1) Not run so as to preserve sample size.
(2) Not run; extreme difficulty with instrument.
*Reproducibility runs.

V. OPTIMIZATION OF ACTIVATION CONDITIONS

A. Method Employed

A successful scheme for optimizing processes with several variables was proposed and developed by Dr. G. E. P. Box of Imperial Chemical Industries, Ltd. in 1955[7] and was simplified by Spendley, Hext and Himsworth, also of ICI, in 1962.[8] The method was originally called "evolutionary operations" but was later labelled "self-directing optimization (SDO)". SDO experiments were reportedly successful in optimizing chemical processes involving several variables (e.g., Maumee Chemical.[9]

The method of employing SDO is mathematically trivial. If n variables are to be optimized, at least n + 1 experiments must be initially performed and at least n + 1 experiments must be retained when some results are rejected during each iteration. The "worst" results are rejected each time. An advantage of the method is that the worst results may be determined in any fashion, even subjectively. The mathematical steps to be taken are as follows:

1. After rejecting one or more runs, average the variables in the remaining runs.
2. Multiply each of the averaged variables times two.
3. In turn, subtract each of the variable values of the rejected run or runs from the doubled corresponding variable. The resulting differences give the new variable quantities for the next run or runs.

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[7] G. E. P. Box, "Evolutionary Operation: A Method for Increasing Industrial Productivity", paper presented to the International Conference on Statistical Quality Control, Paris, July, 1955. Reproduced in Applied Statistics, VI, 1957.

[8] W. Spendley, G. R. Hext, and F. R. Himsworth, "Sequential Application of Simplex Designs in Optimization and Evolutionary Operation", Technometrics, The American Society for Quality Control and The American Statistical Association, Vol. 4, No. 4, November, 1962.

[9] "Maumee moves closer to optimum process to make saccharin", Chemical & Engineering News, 41:76-8, December 9, 1963.

In the case of the activated cloth, four variables (starting material, atmosphere, time, and activation temperature) were to be optimized. Note that each variable should have a numerical value. In this case the CO_2 atmosphere was assigned a value of 1, and steam was assigned a value of 2. Since no mixtures of the two atmospheres were used, the atmosphere for each next run was taken as either 1 or 2 depending on which was closer to the calculated value. The starting material would also have been taken as the nearest integer to the calculated value had fractional results been obtained from the calculations.

B. Results of Optimization Runs

Since four variables were to be optimized, five initial experiments were needed as a minimum number. The thermoset cloth (material No. 9) had not previously been run; therefore, three more runs were added to ensure a more complete matrix. This made a total of eight initial runs which were made.

After making the initial runs, the next problem was to choose the ranking criterion for performance. It was felt that the NARADCOM test should be the final judge of material performance. Therefore, all eight initial samples were sent to NARADCOM for sorptivity measurements. The measured properties of the first eight samples are given in Table 7. NARADCOM measured the sorptivity on an area basis. It was decided to compare results of samples measured according to ASTM D-3467 on a weight basis and on an area basis with NARADCOM results. These comparisons are shown in Figures 7 and 8.

The "r^2" values (coefficients of determination) are measures of the degree to which the data points plotted fit a straight line. The r^2 values also represent a measure of the degree to which the two types of ASTM D-3467 sorptivity values give the same ranking as the NARADCOM values. The correspondence between the ASTM D-3467 sorptivity values and the NARADCOM values is best when area basis measurements are used. Therefore, area basis sorptivities were used for ranking the results of experimental runs.

TABLE 7

RESULTS FROM FIRST OPTIMIZATION SERIES

Run	Material Number	Activation Conditions: Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	Cloth Properties After Activation: CCl_4 Sorptivity(1) (% by Weight)	Breaking Strength(2) (kg)	CCl_4 Activity(1) (mg/cm^2)	NARADCOM Sorptivity (mg/cm^2)
1*	9	1	30	875	0	39	0	0.61
2	10	2	40	900	60	28	10	2.46
3	11	1	50	925	10	16	4	0.15
4	12	2	30	875	47	27	12	3.47
5	9	1	40	900	3	29	2	0.12
6	10	2	50	925	74	15	8	1.23
7*	11	1	30	875	0	26	0	0.08
8	9	2	40	900	72	8.2	9	0.60

*Rejected runs

(1) ASTM D-3467
(2) Measured on 25 mm width

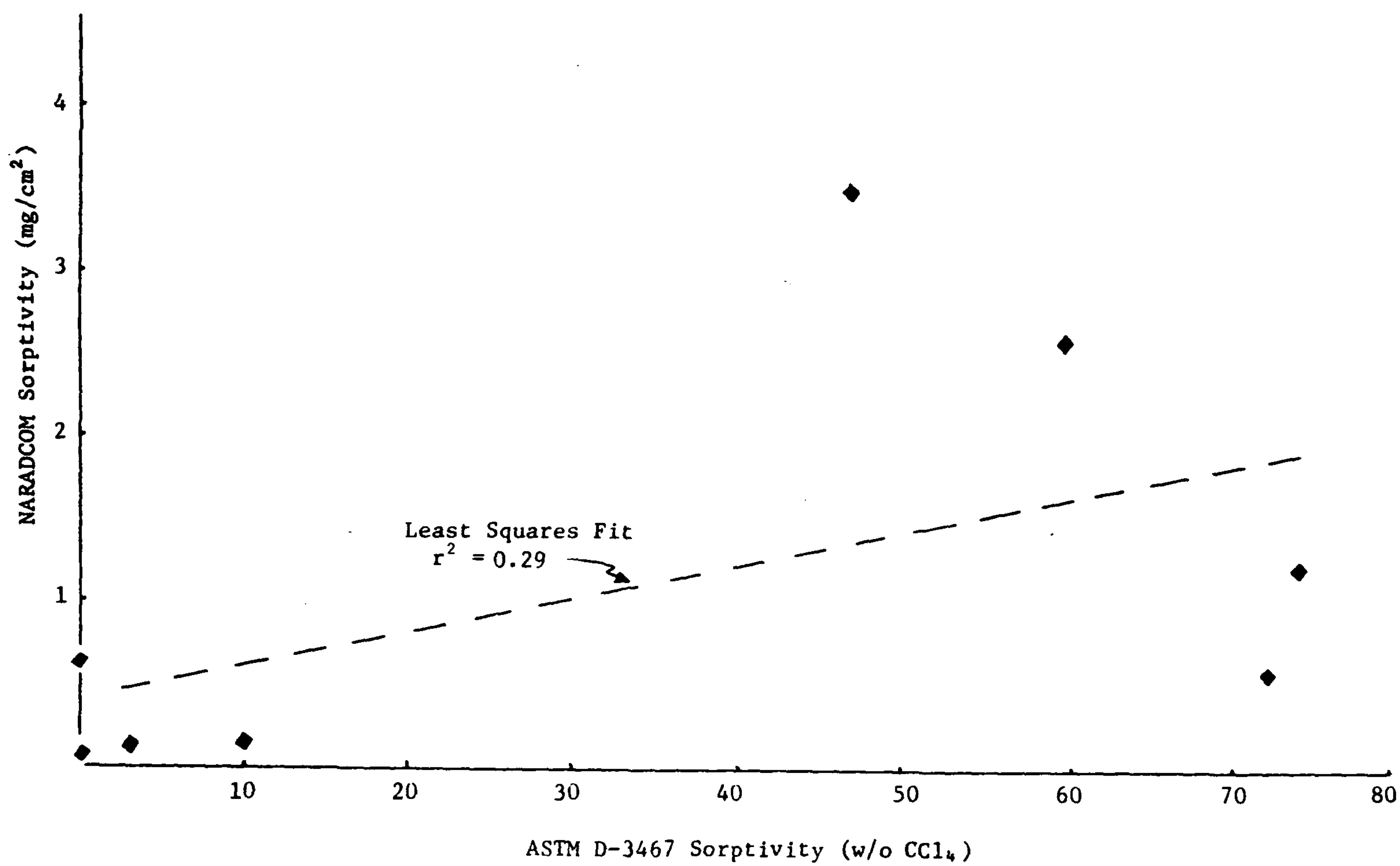

Figure 7. Comparison of NARADCOM versus ASTM D-3467 Sorptivity Values (weight basis), Runs 1 through 8

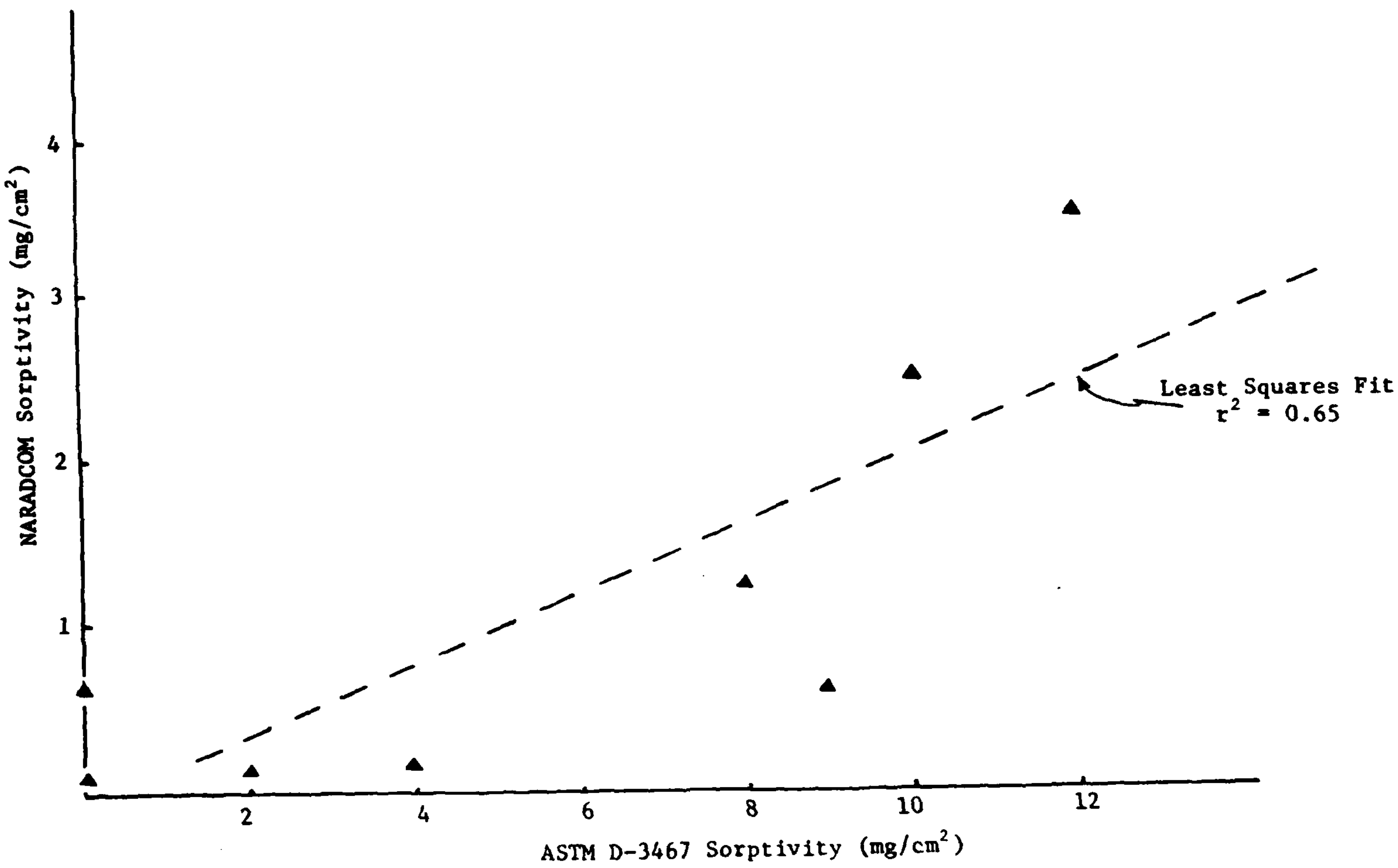

Figure 8. Comparison of NARADCOM versus ASTM D-3467 Sorptivity Values (area basis), Runs 1 through 8

Based on area sorptivities, runs 1 and 7 were rejected from the first group. Table 8 shows the SDO selection process for the conditions for the next two runs. The times, temperatures, and atmospheres are the same for runs 9 and 10. Only the starting materials are different.

Table 9 gives the results of runs 9 and 10, and the selection of conditions for runs 11 and 12. At this point it was decided to backtrack one step and select conditions from the original list of runs based on rejecting those runs which had been found deficient by NARADCOM. Table 10 shows this process. Runs 3, 5, and 7 were rejected and replaced with runs 13, 14, and 15. Table 11 gives the results of the remaining runs through No. 15 and the selection of runs 16 and 17. By this point all runs made with a CO_2 atmosphere had been rejected.

Table 12 gives results of the fourth iteration of the trials. When conditions were calculated for the next two runs, a repetition of previously rejected values was seen. This is normal to the process and means that conditions are converging on an optimum.

Two additional runs were rejected and new conditions were calculated for runs 18 and 19. This is shown in Table 13. Table 14 shows the results of the remaining runs including run 19. At this point it is apparent that run conditions have converged at 875-880°C for about 30 minutes in steam atmosphere. The starting material has shown no preference. Based on the limited data available these conditions should produce materials with sorptivities exceeding 2 mg/cm^2 in the NARADCOM test.

Runs 4, 11, 13, and 19 were chosen as being representative of materials made under optimum process conditions. Additional samples were made under these conditions in runs 20 through 23. Table 15 lists the properties of the samples produced. Those samples were sent to NARADCOM for evaluation.

TABLE 8

SELECTION OF CONDITIONS FOR RUNS 9 AND 10

Starting Material	Atmosphere	Time (min.)	Temperature (°C)	
10	2	42	904	Averages of six best runs
20	4	84	1808	Averages x 2
-9 11	-1 2*	-30 54	-875 933	Minus Run 1
-11 9	-1 2*	-30 54	-875 933	Minus Run 7

Conditions for Runs 9 and 10

(*) Taken at nearest possible condition

TABLE 9

ITERATION 1 OF SDO TRIALS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity(1) (% by Weight)	CCl_4 Activity(1) (mg/cm^2)	Breaking Strength(2) (kg)
2	10	2	40	900	60	10	28
3	11	1	50	925	10	4	16
4	12	2	30	875	47	12	27
5	9	1	40	900	3	2	29
6	10	2	50	925	74	8	15
8	9	2	40	900	72	9	8.2
9*	11	2	54	933	73	9	<2
10*	9	2	54	933	79	3	<2

*Rejected runs

(1) ASTM D-3467
(2) Tested on 25 mm wide strip in warp direction

10	2	42	904	Averages of best runs
20	4	84	1808	Average times 2
-11	-2	-54	-933	Minus Run 9
9	2	30	875	← Run 11 conditions
-9	-2	-54	-933	Minus Run 10
11	2	30	875	← Run 12 conditions

TABLE 10

ITERATION 2 OF SDO TRIALS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity(1) (% by Weight)	CCl_4 Activity(1) (mg/cm^2)	Breaking Strength(2) (kg)
1	9	1	30	875	0	0	39
2	10	2	40	900	60	10	28
3*	11	1	50	925	10	4	16
4	12	2	30	875	47	12	27
5*	9	1	40	900	3	2	29
6	10	2	50	925	74	8	15
7*	11	1	30	875	0	0	26
8	9	2	40	900	72	9	8.2

*Rejected Runs

(1) ASTM D-3467
(2) Tested on 25 mm wide strip in warp direction

10	2	38	895	Averages of best runs
20	4	76	1790	Average times 2
-11	-2	-50	-925	Minus Run 3
9	2	26	865	← Run 13 conditions
-9	-1	-40	-900	Minus Run 5
11	2	36	890	← Run 14 conditions
-11	-1	-30	-875	Minus Run 7
9	2	46	915	← Run 15 conditions

TABLE 11

ITERATION 3 OF SDO TRIALS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity(1) (% by Weight)	CCl_4 Activity(1) (mg/cm^2)	Breaking Strength(2) (kg)
2	10	2	40	900	60	10	28
4	12	2	30	875	47	12	27
6*	10	2	50	925	74	8	15
8	9	2	40	900	72	9	8.2
11	9	2	30	875	45	11	34
12	11	2	30	875	28	10	40
13	9	2	26	865	49	12	21
14	11	2	36	890	66	10	25
15*	9	2	46	915	82	5	<2

*Rejected Runs

(1) ASTM D-3467
(2) Tested on 25 mm wide strip in warp direction

Material Number	Atmos.	Time	Temp.	
10	2	33	883	Averages of best runs
20	4	66	1766	Average times 2
-10	-2	-50	-925	Minus Run 6
10	2	16	841	← Run 16 conditions
-9	-2	-46	-915	Minus Run 15
11	2	20	851	← Run 17 conditions

TABLE 12

ITERATION 4 OF SDO TRIALS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity(1) (% by Weight)	CCl_4 Activity(1) (mg/cm^2)	Breaking Strength(2) (kg)
2	10	2	40	900	60	10	28
4	12	2	30	875	47	12	27
8	9	2	40	900	72	9	8.2
11	9	2	30	875	45	11	34
12	11	2	30	875	28	10	40
13	9	2	26	865	49	12	21
14	11	2	36	890	66	10	25
16*	10 (13)	2	16	841	16	6	41
17*	11 (14)	2	20	851	27	9	46

*Rejected Runs

(1) ASTM D-3467
(2) Tested on 25 mm wide strip in warp direction

10	2	33	883	Averages of best run
20	4	66	1766	Average times 2
-10	-2	-16	-841	Minus Run 16
10	2	50	925	← Repeats Run 6; already rejected
-11	-2	-20	-851	Minus Run 17
9	2	46	915	← Repeats Run 15; already rejected

TABLE 13

ITERATION 5 OF SDO TRIALS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity (1) (% by Weight)	CCl_4 Activity (1) (mg/cm^2)	Breaking Strength (2) (kg)
2	10	2	40	900	60	10	28
4	12	2	30	875	47	12	27
8*	9	2	40	900	72	9	8.2
11	9	2	30	875	45	11	34
12*	11	2	30	875	28	10	40
13	9	2	26	865	49	12	21
14	11	2	36	890	66	10	25

*Rejected Runs

(1) ASTM D-3467
(2) Tested on 25mm wide strip in warp direction

10	2	32	881	Averages of best runs
20	4	64	1762	Average times 2
-9	-2	-40	-900	Minus Run 8
11	2	24	862	← Run 18 conditions
-11	-2	-30	-875	Minus Run 12
9	2	34	887	← Run 19 conditions

TABLE 14

LIST OF FINAL ACCEPTED RUNS

		Activation Conditions			Cloth Properties After Activation		
Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity(1) (% by Weight)	CCl_4 Activity(1) (mg/cm^2)	Breaking Strength(2) (kg)
2	10	2	40	900	60	10	28
4	12	2	30	875	47	12	27
11	9	2	30	875	45	11	34
13	9	2	26	865	49	12	21
14	11	2	36	890	66	10	25
18	11 (14)	2	24	862	30	10	50
19	9	2	34	887	52	11	28
Avgs.	10	2	31	879	50	11	30

(1) ASTM D-3467

(2) Tested on 25 mm wide strip in warp direction.

TABLE 15

PROPERTIES OF FINAL SAMPLES SENT TO NARADCOM

			Activation Conditions			Cloth Properties After Activation	
Run	Reproduces Run	Material Number	Atmos. (#1=CO_2) (#2=H_2O)	Time (Min.)	Temp. (°C)	CCl_4 Activity (% by Weight)	CCl_4 Activity (mg/cm^2)
20	4	12	2	30	875	57	11
21	11	9	2	30	875	46	11
22	13	9	2	26	865	37	11
23	19	9	2	34	887	40	8

VI. RECOMMENDATIONS

The acceptance standards for material currently used by the military in protective clothing[10] requires that the material have a minimum CCl_4 sorptivity of 1.2 mg/cm^2. It appears that pitch-based carbon cloth can be activated to levels beyond that, and further work to develop a production process is merited. The production process should be continuous to avoid nonuniformities which may be introduced in a batch process.

Although the process was optimized by SDO as a single temperature activation, further gains in sorptivity may be realized if a staged or continuously rising heat treatment is used. This possibility should also be explored. Staged thermal treatments are easy to incorporate in a continuous process.

kjd

[10] Military Specification, MIL-C-43858 (GL), Cloth, Laminated, Nylon Tricot Knit, Polyurethane Foam Laminate for Chemical Protection.

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